Picosecond Photon Echoes Detected by Optical Mixing

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PICOSECOND PHOTON ECHOES DETECTED BY OPTICAL MIXING

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Picosecond photon echoes are shown to be easily detected by optical mixing. The synchronized picosecond excitation and probe pulses are generated by amplifying pulses from two dye lasers, synchronously pumped by a mode-locked argon-ion laser. The technique is used to study optical dephasing in the organic mixed crystal of pentacene in *p*-terphenyl.

Photon echo [1] and optical free induction decay [2,3] measurements have been limited to the study of optical dephasing processes that occur on a nanosecond time scale.

Several interesting dephasing processes as exciton [4] and polariton [5] scattering and vibrational dephasing [6] however occur on a picosecond time scale and study of these phenomena therefore necessitates usage of picosecond excitation pulses and detection techniques.

Recently it has been shown that the dephasing of coherently excited molecular vibrations can be measured by probing the intensity of the coherent anti-Stokes Raman scattering as a function of the delay between the excitation and probe pulse [7]. The same probe technique was also employed in a study of the two-photon induced coherence in calcium vapor [8]. This picosecond pulse-probe technique however is not expected to be applicable to a study of electronic dephasing processes in solids.

In this letter we report a simple yet versatile picosecond laser technique that should be useful in the study of coherent optical transients in solids and gases. In this technique the picosecond coherent transient, e.g. photon echo, is *optically mixed* [9] with a picosecond probe pulse. The coherent transient is then observed at the sum frequency (or difference frequency if desired) of the excitation and probe laser frequency. The idea to use frequency up-conversion for picosecond optical sampling was first suggested by Dugay and Hansen [10], and recently applied by Mahr and Hirsch [11] and Hallidy and Topp [12]. Moreover the experiments may be done at repetition rates (10—100 Hz) that enable usage of efficient electronic signal averaging techniques.

We demonstrate the utility of the technique in a study of picosecond photon echoes in the organic mixed crystal of pentacene in *p*-terphenyl. The conclusion is that up to 12 K, optical dephasing is only caused by scattering off a pseudo-local phonon with a frequency of 28 ± 2 cm^{-1} and a lifetime of ca. 3 ps.

Fig. 1 shows that the whole experimental arrangement is centered around two dye lasers (at different frequencies) which are synchronously pumped [13] by a mode-locked argon-ion laser. The argon-ion pump laser (Spectra Physics model 171-03) equipped with a 20% output coupler, is mode-locked with an acousto-optic modulator driven by an ultrastable oscillator (HP 608F signal generator with 8708A synchronizer). The output (900 mW average power at 514.5 nm, 110 ps pulses) is split by a 30% reflecting beamsplitter. The transmitted beam is used to pump a Spectra Physics 375 dye laser (DL 2) with rhodamine (Rh) 6G and Rh 101 (each 1.5×10^{-3} mol/ℓ in ethylene glycol) as active medium. The dispersive element is a seven layer wedge. With the reflected part of the argon laser beam a Coherent Radiation 590 dye laser (DL 1) is pumped (Rh 6G, 4×10^{-3} mol/ℓ in ethylene glycol) equipped

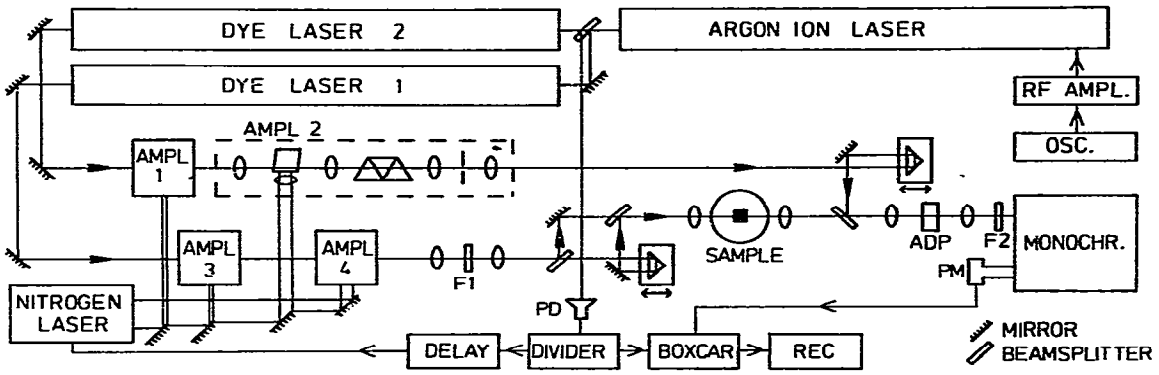

Fig. 1. Experimental arrangement for picosecond photon echo studies. For a detailed description of the set-up consult the text. PD: photodiode, PM: photomultiplier, F1: Corning 2-60 filter, F2: Corning 7-54 filter.

with a two element birefringent filter. In most experiments reported here additional etalons (FSR 900 GHz) were placed in both dye laser cavities. Under these conditions both dye lasers produced transform limited pulses of 18 ps (0.9 cm^{-1} bandwidth) as determined in autocorrelation measurements [14]. The average power is 25 mW. The jitter between the two pulse trains was determined in a cross-correlation experiment [11] by mixing the two beams in an ammonium dihydrogen phosphate (ADP) crystal. Under optimum conditions we find in agreement with a recent report [15] a jitter of 8 ps. More typically however a jitter of 25 ps is obtained.

Fig. 1 further shows that selected pulses out of each pulse train are amplified using a 400 kW nitrogen laser [16] (Molectron UV 400). Synchronization is achieved by monitoring the argon laser pulse train with a fast photodiode (HP 5082-4220). The obtained 80 MHz signal is divided and, after suitable delay, used as trigger for the nitrogen laser. Two amplification stages are used for each dye laser. A stage consists of a magnetically stirred dye cell and a prism spectral filter (bandwidth 5 Å). Dye cell 1 (5×10^{-3} mol/ℓ Rh B in ethanol) and 3 (2.5×10^{-3} mol/ℓ Rh 6G in ethanol) are each pumped by 15% of the nitrogen laser output power, dye cell 2 (5×10^{-3} mol/ℓ Rh B in ethanol) and 4 (5×10^{-3} mol/ℓ Rh 6G in ethanol) by 35% each.

The nitrogen laser is focused in the dye cells by a combination of spherical and cylindrical lenses. The final filtering of the excitation beam is done by focusing through a Corning 2-60 filter which acts as a saturable absorber. The outcoming beam has a perfect TEM_{00} mode structure while the unamplified pulses are in intensity down by at least a factor of 10^7.

Both laser pulses have a peak power of 40 kW while no broadening in time or frequency is observed.

In the picosecond photon echo experiment on pentacene in *p*-terphenyl now to be described the excitation dye laser (DL-1) is tuned to the origin of the lowest electronic transition of pentacene of site O_1 at 592.16 nm while the probing dye laser is tuned to the wavelength for maximum output (637 nm). To generate the photon echo the excitation pulse is split and after a delay recombined to get the desired two pulses. With neutral density filters the intensity ratio of first and second pulse is set to 1:4. Both beams are then focused on the sample which is inside a temperature variable cryostat. The sample preparation and cryostat characteristics have been described in a previous paper [17]. After passing through the sample the excitation pulses and the echo are combined with the probe pulse via a 50% beamsplitter.

The collinearly aligned beams are focused with a 15 cm lens in a 15 mm ADP crystal, angle tuned for phase matching at the sum frequency of the two dye lasers. The probe pulse is delayed to coincide with the echo. With a Corning 7-54 filter the excitation and probe pulses are blocked, while the up-converted echo is detected via a 3/4 m Spex monochromator with a Philips 150 UVP photomultiplier at 307 nm. The signal is either displayed on a Tektronix transient digitizer or processed using a PAR boxcar integrator with a digital storage option.

With the set-up described we have been able to de-

tect picosecond photon echoes of pentacene in *p*-terphenyl using excitation pulse separations down to 50 ps.

The following tests were done to show that the observed frequency up-converted echo signals were genuine.

Firstly, the echo signal is detected at the calculated time.

Secondly, the echo signal is only observed when all three pulses (two excitation and one probe) are simultaneously present.

Thirdly, the echo signal is only observed when the excitation laser is tuned to the absorption of pentacene.

In fig. 2 we have displayed an up-converted time-resolved echo signal of pentacene in *p*-terphenyl at 1.5 K. The signal is obtained by recording the echo signal from the boxcar integrator, while slowly varying the delay between the probe pulse and the echo. Note that the width of the cross-correlation between the photon echo and probe pulse is identical to the width of the cross-correlation between the excitation and probe pulse which implies that the echo width (in time) is still determined by the excitation pulse width. With shorter pulses the echo width will be determined by the absorption linewidth ($\approx 1\ \mathrm{cm}^{-1}$).

The up-converted echo signal is used to study optical dephasing of pentacene in *p*-terphenyl and in fig. 3 the intensity of the photon echo as a function of temperature is given for two excitation pulse separations. Note that with 100 ps separation between the excitation pulses the photon echo is still detectable at 12 K.

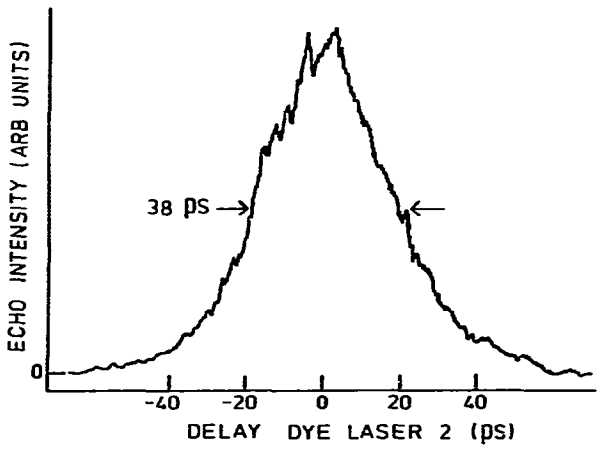

Fig. 2. Cross-correlation measurement at 2 K between the photon echo of pentacene in *p*-terphenyl and the probe pulse, detected at 307 nm.

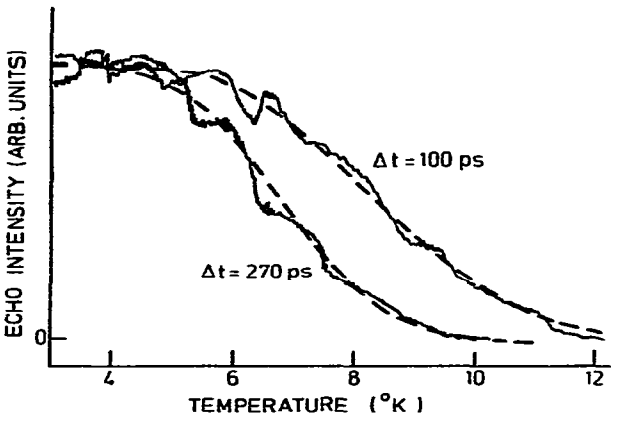

Fig. 3. Temperature dependence of the photon echo intensity of pentacene in *p*-terphenyl at two excitation pulse separations (Δt). The dashed lines are theoretical curves assuming $T_2(T) = k_\infty \exp(\Delta E/kT)$ with $\Delta E = 28 \pm 2\ \mathrm{cm}^{-1}$ and $k_\infty = 3 \pm 1.5$ ps.

With nanosecond pulses the echo could only be detected up to 4 K [17]. Above 10 K optical dephasing of pentacene in *p*-terphenyl may be studied using high-resolution absorption spectra [18].

The noisy curves in fig. 3 are experimentally obtained while the dashed curves are fittings whereby the optical dephasing time (T_2) is assumed to exhibit the following temperature dependence $T_2(T) = k_\infty \exp(\Delta E/kT)$ [17]. Hereby is $\Delta E = 28 \pm 2\ \mathrm{cm}^{-1}$ and $k_\infty = 3 \pm 1.5$ ps. We first note that these constants also fit the nanosecond photon echo relaxation behaviour of pentacene [18], whereby it is demonstrated that the coherence bandwidth of the excitation laser has no effect on optical dephasing in this molecule [19]. The observed exponential activation of T_2 with temperature up to 12 K indicates that optical dephasing of pentacene in *p*-terphenyl is only caused by scattering processes that involve a pseudo-local phonon mode. Additional line-broadening and line-shift data are presently taken [18] to decide whether Raman-like scattering [20] and/or optical exchange [21, 22] is responsible for the observed dephasing. It is quite interesting however to note that up to 12 K the contribution of the bulk phonons to optical dephasing is negligible.

It seems worth mentioning that photon echoes of

pentacene were also easily observed using 10 ps excitation and probe pulses. We note that with the power density used in the latter experiment (ca. 1 GW/cm^2) no crystal surface damage was observed. It therefore seems plausible that coherent optical effects in organic materials at low temperature may be studied using pulses as short as a few picoseconds.

In the technique presented the synchronism of the probe pulse with the echo is the main limitation to increased time-resolution in the experiments. With the second harmonic and fundamental of a picosecond laser as excitation and probe pulse this problem is absent. As an alternative, a stimulated Raman pulse might be used as a probe.

In conclusion then it seems that (sub) picosecond optical coherent transients may be conveniently studied by optical mixing.

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